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Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling

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Statement of Problem and General Approach: Long-term sequestration of uranium at sites within the DOE complex is a significant problem that requires molecular-level information on the speciation, phase association, and spatial distribution of uranium. Designing remediation/sequestration strategies relevant to complex natural systems requires studies of uranium speciation and interactions in simplified model systems as well as in the natural systems. We have used this coupled approach to conduct molecular-level studies of the speciation and phase association of uranium in the vadose zones of Hanford Area 200 and Area 300 sites as well as in model systems designed to understand how U(VI) adsorbs to mineral surfaces.

Speciation of Uranium in the Hanford Area 200 Vadose Zone: Contamination of vadose zone sediments under tank BX-102 at the Hanford site, WA, resulted from the accidental release of 7 to 8 metric tons of uranium dissolved in caustic aqueous sludge in 1951. We have applied synchrotron-based X-ray spectroscopic and diffraction techniques to characterize the speciation of uranium in samples of these contaminated sediments [Catalano *et al.*, *Environ. Sci. Technol.* 38, 2822, 2004]. U L_{III}-edge X-ray absorption fine structure (XAFS) spectroscopic studies demonstrate that uranium occurs predominantly as a U(VI)-silicate from the uranophane group of minerals. XAFS cannot distinguish between the members of this mineral group due to the near identical local coordination environments of uranium in these phases. However, these phases differ crystallographically, and can be distinguished using X-ray diffraction (XRD) methods. As the concentration of uranium was too low for conventional XRD to detect these phases, X-ray microdiffraction (μXRD) was used to collect diffraction patterns on ~20 μm diameter areas of localized high uranium concentration found using micro-scanning x-ray fluorescence (μSXRF). Only sodium-boltwoodite, $Na(UO_2)(SiO_3OH)\cdot 1.5H_2O$, was observed; no other uranophane group minerals were present. In addition, J.G. Catalano was part of a collaboration with PNNL scientists that used a combination of optical fluorescence spectroscopy and EXAFS spectroscopy to characterize U(VI)-containing silicates in the Hanford vadose zone

(Wang *et al., Geochim. Cosmochim. Acta* **69**, 1391, 2005). In summary, sodium-boltwoodite formation has effectively sequestered uranium in these sediments under the current geochemical and hydrologic conditions. Attempts to remediate the uranium contamination will likely face significant difficulties because of the speciation and distribution of uranium in the sediments.

Speciation of Uranium in the Hanford Area 300 Vadose Zone: The disposal of basic sodium-aluminate and acidic U(VI)-Cu(II) wastes into the now-dry North and South 300 A Process Ponds at the Hanford site resulted in a U(VI) groundwater plume. To gain insight into the geochemical processes that occurred during waste disposal and that will affect the future fate and transport of this uranium plume, the solid-phase speciation of uranium in a depth sequence from the base of the North Process Pond through the vadose zone to the water table was investigated using electron microprobe measurements and XAFS spectroscopy [Catalano *et al., Environ. Sci. Technol.* **40**, 2517, 2006]. Uranium in sediments from the base of the pond was predominantly co-precipitated with calcite. From ~2 m below the pond base to the water table uranium occurred dominantly in a sorbed form, likely on the surface aluminosilicate clay minerals. The presence of a U(VI)-phosphate phase was also observed in this region, but it only occurred as a major uranium species at one depth. The initial sequestration of U(VI) in these sediments likely occurred through co-precipitation with calcite as conditions did not favor adsorption. As the calcite-bearing pond sediments have been removed as part of a remediation effort, future uranium fate and transport will likely be controlled primarily by adsorption/desorption phenomena.

Model System Studies: In addition to a detailed XAFS study of uranyl environments in a wide variety of crystalline model compounds [Catalano and Brown, *Am. Mineral.* **89**, 1004, 2004], we have also conducted a series of model system studies in which the interaction of U(VI) with various mineral surfaces has been examined using synchrotron-based x-ray spectroscopy and x-scattering experiments. In bulk XAFS studies of the interaction of U(VI) with a Wyoming montmorillonite (SWy-2) under atmospheric conditions [Catalano and Brown, *Geochim. Cosmochim. Acta* **69**, 2995, 2005], we found that U(VI) forms dominantly outer-sphere complexes at pH 4 and an ionic strength of 10^{-3}M, consistent with binding in cation exchange sites. In contrast, at pH 7 and an ionic strength of 1M, we found that U(VI) binds dominantly in an inner-sphere fashion to edge sites, most likely as uranyl-carbonato complexes bound primarily to $Fe(O,OH)_6$ sites rather than $Al(O,OH)_6$ sites. In another study [Catalano *et al., Geochim. Cosmochim. Acta* **69**, 3555, 2005] we carried out a combination of GI-XAFS and crystal truncation rod diffraction measurements on U(VI) complexes on hydrated α-Al_2O_3 (1-102) and α-Fe_2O_3 (1-102) surfaces, which have similar surface structures. On both surfaces we found that uranyl-carbonato complexes form. However, the mode of binding is dominantly monodentate on the α-Al_2O_3 (1-102) surface and dominantly bidentate on the α-Fe_2O_3 (1-102) surface. Both XPS and CTR diffraction showed higher U(VI) surface coverages on α-Fe_2O_3 (1-102) than on the α-Al_2O_3 (1-102) surface. In addition, the surface complexes observed are different from the bidentate mononuclear complexes that are typically derived for U(VI) on powdered Al- and Fe-(oxyhydr)oxide surfaces. In addition to this work, Jeffrey G. Catalano, a Stanford University Ph.D. student in Gordon Brown's research group who was supported by this grant, participated in two additional model system projects that were related to this grant. One involved the synthesis and characterization of sodium meta-autinite, a possible solid precipitate in the Hanford Vadose Zone (Wellman *et al., Radiochim. Acta* **93**, 393, 2005). A second

involved determination of solid UO_2 dissolution kinetics (Pierce *et al., J. Nuclear Materials* **345**, 206, 2005).

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9. E.M. Pierce, J.P. Icenhower, R.J. Serne, and J.G. Catalano (2005) Experimental determination of UO_2(cr) dissolution kinetics: Effects of solution saturation state and pH. *J. Nuclear Materials* **345**(2-3), 206-218.